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Interactive comment on “Air–water fluxes and sources of carbon dioxide in the Delaware Estuary: spatial and seasonal variability” by A. Joesoef et al.

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Anonymous Referee #2

— We first want to thank you for the very thorough and constructive reviews. These suggestions have greatly strengthened the overall flow and organization of the manuscript. The positive encouragement to expand on certain sections that needed additional explanation or supporting evidence has significantly improved the clarity of the paper and reinforced the validity of our results. Taking all your suggestions into consideration, we have made great efforts to strengthen the methods section, incorporate variability statistics to Table 1 (now Table 2), and expand on why this specific

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CO₂ study (the Delaware Estuary) is so important. In addition, to help address the uncertainties and limitations to our study, we have composed a new assumptions and limitations section (4.4).

— Major Comments

— In calculating temperature-normalized pCO₂, it is necessary to define an annual mean temperature against which seasonal fluctuations can be measured. Here, the authors use the mean water temperature measured in the Delaware Estuary from 2013-2015, which covers the span of their sampling. Others have adopted a more climatological approach that uses a long-term annual mean temperature, as may be provided by the 10-year average temperature cycle the authors show in Figure 3. Especially since there important seasonal gaps in the authors' analysis (e.g., January and February - the two lowest temperature months), it is my instinct to suggest using a more resolved temperature product for this calculation, such as a USGS record (e.g., that given in Figure 3a if it can be applied to the entire estuary) or a satellite-derived mean. If the authors used a similar temporal interpolation to get an annual temperature despite months without data (as in the calculation of annual CO₂ fluxes including months without data, which could also be better shown and described itself), this should be more directly stated. A broad recalculation of this result constitutes a major revision.

Agreed. In order to obtain a more solid representation of the annual mean surface water temperature in the Delaware Estuary against which seasonal fluctuations can be measured, a longer annual record (10-yr average) of surface water temperature cycles would be more appropriate. This would help smoothen out any anomalies that a shorter record would have trouble accounting for. Thus, I have decided to use the 10-year average temperature (13.3°C) as shown in Figure 3a for the annual mean surface water temperature in my calculations.

— Throughout the description of their techniques, the authors take care to point out

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weaknesses. However, they provide no systematic error analysis. A consolidated summary of methods, assumptions, caveats and gaps at least is integral to the readers understanding, and what was missed. For example, I was left wondering how the salinity-binned temperature-normalized pCO₂ related to the area-averaged CO₂ flux. This seemed out of place next to the other area-based considerations (e.g., Tables 1 and 2, Figures 8 and 9), and the implications of this choice were not well explained either for the method itself or for the interpretation of the data. For additional examples, see the annual mean temperature choice highlighted above, and the absence of discussion about any weakness in the river CO₂ contribution calculations, as well as additional points listed in the minor comments below. I consider additional discussion of assumptions and caveats a major revision, whether it involves additional text or additional calculations.

To resolve these comments, I highly recommend that the authors include a conceptual sketch to summarize their calculations, and consolidate the information about their assumptions and caveats in a clear, concise additional section. An excellent reference would be the recent manuscript published by W. Evans and colleagues, which required a similar methodological description and error calculation to underpin their observations of coastal CO₂ fluxes. See <http://onlinelibrary.wiley.com/doi/10.1002/2015GB005153/abstract>.

Taking your responses into consideration, I have added a new assumptions and caveats section (4.4) to better address the various limitations in our study.

4.4 Assumptions and limitations

“While this study serves as the first air-water CO₂ flux product in the Delaware Estuary, there are several limitations. First, the lack of cross-bay transects (east to west), except in December 2014, limits our knowledge of surface water pCO₂ distributions in shallow waters regions of the bay system. Due to various biological and physical processes (i.e. influence from nearby tidal marshes, tributaries, or estuarine circulation forces),

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surface water pCO₂ may vary from within the main channel to the perimeters of the estuary. Jiang et al., (2008a) found that surface water pCO₂ and air-water CO₂ flux in the marine-dominated Sapelo and Doboy sounds paralleled seasonal temperature changes and net CO₂ inputs from within the estuarine zone. Due to intense productivity of vegetation in the surrounding salt marshes, extensive accumulation of organic carbon occurs during spring and early summer (Dai and Wiegert, 1996; Jiang et al., 2008a). During late summer and early fall, increased surface water temperatures coupled with tidal flushing of intertidal marsh waters and the decomposition of dead plants contribute to high CO₂ degassing in these estuaries (Dai and Wiegert, 1996; Cai and Wang, 1998; Cai et al., 1999; Neubauer and Anderson, 2003; Wang and Cai, 2004). However, due to the much broader geographic size of the Delaware Bay compared to the marine-dominated Sapelo and Doboy sounds, in-water biological processes are most likely important. In turn, the impact from the growth and decay of marsh plants on surface water pCO₂ and CO₂ flux dynamics may not be as influential in the Delaware Bay except near the shorelines where tides regularly flush marsh boundaries. Studies conducted by Culbertson et al., (1987) and Lebo et al., (1990) performed several cross bay transects sampled at various depths, over diel cycles, within tributaries, and periodically offshore. Results showed that cross-bay gradients were inconsistent and relatively small, except in shallow waters near the shoreline when total suspended sediment and chlorophyll concentrations were frequently elevated (Culbertson et al., 1987; Lebo et al., 1990; Sharp et al., 2009). Thus, the impact from marsh input of DIC to the Delaware Bay on overall pCO₂ distributions and associated CO₂ degassing fluxes are most likely small. During December 2014, pCO₂ measurements were not only collected in the main channel, but also near the Delaware and New Jersey perimeters of the bay (Fig. 6I). While slight variability was observed across the bay, pCO₂ values from the lower to upper bay regions remained within about 150 μ atm (Fig. 6I and Table 2).

In addition to the lack of cross bay transects, there is a pressing need to conduct more winter and early spring surveys to fully cover seasonal ranges in key properties such

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as temperature and river discharge rates. Moreover, cruises or moored sensor studies at or around large discharge events are needed. Recent study by Voynova and Sharp (2012) found that in the past century there have been a recorded 54 extreme discharges (defined by the average daily discharge as recorded in Trenton, NJ from 1 Oct 1912 to 30 Sept 2011 plus 10 standard deviations); 46% of these occurring in the past decade (Voynova and Sharp, 2012). With increasing evidence suggesting that extreme weather events will occur more frequently with climate change, it is important to maintain routine seasonal surveys to learn how such subsequent conditions (i.e. increased summer stratification, riverine CO₂ fluxes, removal of oxygen in bottom waters) impact various coastal environments (Allan and Soden, 2008; Yoana and Sharp, 2012). Furthermore, more research is needed in the urban and upper river sections of the estuary to better understand CO₂ dynamics throughout the whole estuarine gradient. The lack of inorganic carbon data in these upper regions limits syntheses of regional CO₂ fluxes and generalizations to underlying mechanisms. Routine sampling along small tributaries and river systems could provide crucial insight to the biogeochemistry in the upper tidal river.

There are also several limitations to the temperature-normalized and end-member mixing models that need to be addressed. First, knowing the extensively complex nature of estuarine systems, it is important to note that derived variances in temperature-normalized pCO₂ provide only a relatively simple analysis of seasonal pCO₂ fluctuations due to thermal and non-thermal processes as it neglects the impact that various physical processes, turbulent forces, and tidal mixing scenarios have on pCO₂ dynamics. However, because salinity gradients down the estuary vary greatly depending on the season, river discharge, tidal cycle, precipitation, and other circulation processes, salinity-binned climatologies can provide additional insight to the various physical and biological controls behind observed pCO₂ distributions that geographic boundaries may not. Unfortunately, due to the lack of winter surveys and unusually high pCO₂ values in December, interpolated temperature-normalized pCO₂ during cooler months may be biased and slightly overestimated. Moreover, the temperature derived con-

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stants ($\partial \ln p\text{CO}_2 / \partial T$) derived in this study were based on river and ocean end-member TA and DIC concentrations collected in the Delaware Estuary over the past two years. Thus, it is important to note that derived temperature constants here are applicable for general estuarine systems and may not be suitable for coastal environments with different hydrological and/or geochemical characteristics.

In situ DIC and TA measurements were coupled using the Excel macro CO2SYS (Pierrot, 2006) and inorganic carbon dissociation constants from Millero et al. (2006) for estuarine waters to calculate dissolved CO₂ concentrations. While river and ocean end-members were obtained at near zero salinity and at the mouth of the bay, respectively, no fixed end-member sampling locations were established. This marginal difference in end-member location could slightly increase or decrease estimated CO₂ concentrations. In the chemical model of the CO2SYS, NH₃, NH₄⁺, and organic matter contribution to TA were not included (Cai et al., 1998; Cai et al., 2010b), which were likely high in low salinity waters. Thus, lower calculated CO₂ than observed CO₂ was expected as the observed TA included other acid-base components (Fig. 3C). However, due to the very high pCO₂, such uncertainty is deemed unimportant in our consideration. Another factor that may contribute to the lower calculated CO₂ than observed CO₂ could be the use of mercuric chloride as a preservative in low salinity samples (*S* < 10) (Trabalka and Reichle, 2013). Excess alkalinity generated via the dilution of mercuric chloride could contribute to conservative CO₂ flux estimates (Trabalka and Reichle, 2013) although due to the relatively high TA in the Delaware River we believe this effect is small.”

— Minor Comments

— Introduction

— Page 10900 Line 24: Nice note about industrialization and future change at the end of this manuscript that could be included up front.

Thanks. I wanted to emphasize the point that the system is continuously responding to

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a rapidly changing environment (i.e. industrialization) and have moved this part and added some supporting evidence to the Introduction.

“The tidal freshwater portion of the Delaware River flows from the head of the tide near Trenton, NJ through the greater Philadelphia area, the sixth largest municipal region of the U.S., before passing into the saline Delaware Bay (Fig. 1) (Sharp et al., 2009; Sharp, 2010). In turn, the upper Delaware River is heavily influenced by major industrial activity and continuously responding to a rapidly changing environment. For example, in the mid-20th century, the urban river of the Delaware Estuary suffered from severe hypoxia with average summer dissolved oxygen (DO) concentrations near zero value (Sharp, 2010). Fortunately, the implementation of the Clean Water Act (CWA) in the early 1970s helped promote efforts to improve water quality conditions in the Delaware River. With major upgrades to large sewage treatment plants, DO concentrations since the early 1990s have consistently been above the CWA standard of 3.5 mg L⁻¹ (~219 μ mol L⁻¹) illustrating significant recovery from post hypoxic conditions (Sharp, 2010). Nonetheless, high pCO₂ is still expected to associate with strong respiratory O₂ consumption in the upper estuary. In contrast, the Delaware Bay is a large shallow embayment surrounded by partially undeveloped salt marshes (Cifuentes et al., 1988). Thus, the Delaware Estuary is governed by the dynamic interaction between a river dominated upper estuary and an ocean dominated lower bay. This feature, typical for other large estuaries, and depending on river flow and geomorphology, smaller estuarine systems as well, provides us the opportunity to examine how contrasting geographical settings, physical mixing processes, and ecosystem metabolism in an extensive bay system can affect CO₂ gas exchange.”

— Page 10902 Line 5/6: Great statement. Lead this section with that, and then clearly state the gaps that contribute to this concern (spatially, not a lot done in Mid-Atlantic; theoretically, not a lot done in large, fast-moving estuaries), and how the Delaware Estuary could help address these issues. That would lead well into the review of the Delaware R. Estuary in the next section.

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This paragraph now leads as follows:

“There is rising concern that global estuarine CO₂ degassing flux may be overestimated (Cai, 2011). Although substantial progress has been achieved over the past decade (Borges and Abril, 2011; Chen et al., 2013; references therein), our knowledge of CO₂ degassing fluxes and their controlling processes in estuaries remains insufficient. Globally, the majority of past estuarine CO₂ studies have been conducted on small estuarine systems, which typically have high pCO₂. (Chen and Borges, 2009; Cai, 2011; Borges and Abril, 2011). . .”

In addition, I have added the following to address the importance and lack of CO₂ studies conducted in the Delaware Estuary:

“ . . . Thus, there is limited research on CO₂ dynamics in large estuaries or bay systems with long freshwater residence times in the U.S. Mid-Atlantic coast (most notably the Chesapeake and Delaware estuaries). Presumably, these large estuaries have lower pCO₂ than small estuaries or bay systems with rapid freshwater transit times (Borges and Abril, 2011; Cai, 2011). Except for a few recent studies and the pioneering work of Sharp and Culberson, over the past 30 years there have been few inorganic carbon studies in the Delaware Estuary (Culberson, 1988; Sharp, 2009). Air-water CO₂ fluxes, total DIC fluxes, and ongoing evaluations of water acidification have not been consistently (via annual and seasonal surveys) studied. Overall, there is a lack of data and pressing need to synthesize and expand global research to larger estuaries. Furthermore, of past estuarine CO₂ studies, many lack spatial and seasonal coverage of surface water pCO₂ and air-water CO₂ fluxes, making flux estimates highly uncertain.”

— Page 10902 Line 9/10: Later you point out that your manuscript represents the first carbon work, so it is important here to state that too.

In addition to the added information above about the lack of inorganic carbon studies in the Delaware Estuary, I have stated that this is the first paper that summarizes a CO₂ flux product for the system.

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“In this paper, we report the first seasonal distribution of pCO₂ and air-water CO₂ flux in the Delaware Estuary, which was surveyed nine times via various day- to week-long surveys from 2013 through 2014. We further assess the temperature and biological effects on pCO₂ distributions as well as the overall contribution of internal versus riverine sources on CO₂ inputs to the estuarine system. Finally, we present a summarized pCO₂ distribution over the study area and provide a conceptual model to illustrate the control mechanisms on surface water CO₂ dynamics in the Delaware Estuary.”

— Page 10902 Line 14: Why does industrialization matter? It is better stated at the conclusion of the paper, but should be explained here too.

Agreed. Please see above response (Page 10900 Line 24) where I address industrialization and the systems continuous response to a rapidly changing environment (with historical examples).

— Page 10903 Line 3: Sampling bias implied by lack of Jan/Feb data. This should be discussed in reorganized methods section.

The lack of winter data definitely limits our seasonal coverage of the system. I've tried my best to address this issue in the new caveats section (please see 4.4 Assumptions and limitations)

— Methods

— Page 10904 Line 3/4: Sampling method reference for filtration?

The same sampling technique as in Cai and Wang (1998) and Jiang et al. (2008a) was used. I have added these references. When collecting water, all bottles were overflowed for at least twice its volume to minimize contact with the atmosphere.

— Page 10904 Line 5: There is some internal discussion among the carbon community about use of mercuric chloride as a preservative in low-salinity samples. The challenge is that the mercury salt impacts alkalinity concentrations at salinities less than 10. The excess alkalinity from the HgCl₂ may have lowered calculated CO₂ concentrations,

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and as a result these k estimates are likely conservative. Important to point this out in new assumptions/caveats section.

Please see new 4.4 Assumptions and limitations section. As mentioned earlier, due to the relatively high TA in the Delaware River, we believe this effect is small.

— Page 10904 Line 26: Starting out this section strong by trying stating these challenges directly, but need a clearer description or summary of how they were addressed.

To address the challenge of estimating gas transfer velocities, we adopted an established method based on wind speed that avoided calculations of zero gas transfer velocities (k) at low wind speeds (Wanninkhof et al., [2009]).

“Unfortunately, because there have not been many studies on gas transfer velocities in estuaries, we relied on wind speed dependence to estimate gas exchange rates. . . To avoid gas transfer velocities of zero in river and inland waters where wind speeds are typically low, we adopted the gas transfer relationship as proposed by Wanninkhof et al., (2009). . .”

In order to address the challenge of obtaining spatial and temporal heterogeneity of pCO₂ distributions I added the following details:

“Another challenge to accurately determining air-water CO₂ fluxes is obtaining reliable spatial and temporal pCO₂ distributions. Unfortunately, while seasonal distributions of pCO₂ were measured from the mouth of the bay to near zero salinity of the estuary (north to south), our lack of cross bay transects (east to west) limits our knowledge of CO₂ dynamics in shallow water regions of the estuary. Thus, there is a pressing need to conduct more research near these shallow water boundaries”

— Page 10906 Line 14: Why split the upper and mid-bay regions? Are these salinity binned designations, or geographically...?

We noticed rapid changes and range in pCO₂ values (salinity as well) across these regions and felt that if we divided the area into one more region (now upper, mid-, and

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lower bay) that this would allow for a more thorough comparison of pCO₂ and CO₂ fluxes throughout the system.

Geographically binned designations

“In order to calculate area-averaged CO₂ flux throughout the Delaware Estuary, the system was divided into five geographic zones as defined by Sharp et al. (2009). However, due to rapid change in pCO₂ values across the mid-bay, this region was split into an upper and mid-bay zone to allow for a more robust comparison of pCO₂ and CO₂ fluxes throughout the system (Fig. 1).”

— Page 10907 Line 24: stating the temperature constant here is redundant “Similar to the results found in Jiang et al. (2008a), temperature derived constants were lower than the isochemical seawater constant 0.0423°C⁻¹ determined by Takahashi et al. (1993)”

This is now replaced with, “Similar to the results found in Jiang et al. (2008a), temperature derived constants were lower than that determined by Takahashi et al. (1993).”

— Page 10907 Line 25-27: Address with other caveats in new section Thus, knowing the extensively complex nature of estuarine systems, it is important to note that derived variances in temperature-normalized pCO₂ provide only a relatively simple analysis of seasonal pCO₂ fluctuations due to temperature and biological processes as it neglects the impact that various physical processes, turbulent forces, and tidal mixing scenarios have on pCO₂ dynamics.

I have addressed this issue and other caveats in new limitations section (please see 4.4 Assumptions and limitations)

— Page 10908 Line 13: Not sure what “stationary” signifies here. The salinity bin rationale needs more detail, and more description of how salinity-bins and geographic bins relate to each other in the data interpretation. — Page 10914 Line 6: Why is the salinity interval more important than the geographical interval? I’m still confused by the

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salinity binning as described in Section 2.3 and the results here are not helping clarify why this was important or what it showed.

“Stationary” has been removed as it only brought confusion and is unnecessary. More information on the difference and importance between salinity and geographic bins has been added.

“Because salinity gradients down the estuary vary greatly depending on the season, river discharge, tidal cycle, precipitation, and other circulation processes, salinity-binned climatologies can provide crucial insight and a different perspective to the various physical and biological controls behind observed pCO₂ distributions that geographic boundaries may not. In turn, pCO₂ values from each survey were constructed into salinity-binned climatologies (intervals of five units from 0-30) to better isolate and interpret the thermal versus non-thermal effects on seasonal pCO₂ fluctuations.”

— Page 10909 Line 20-22: Clever way of calculating this, but is it the ideal way? What are the challenges here? Good thing to discuss in caveats section.

Discussed some limitations of using TA and DIC to calculate CO₂ in new caveats section.

— Page 10910 Line 15: Very interesting comment in the caption for Figure 2 concerning panel C, but panel C is not discussed here. Another important point for the assumptions and caveats section, especially since CO₂SYS was again used for the calculation of riverine contribution to ĦĆuxes (Section 2.4; Page 10909, line 20-22).

I included part of the caption into the main paper to assist with clarification. In addition, I have added some discussion about assumptions and limitations in this part to the new caveats section. I have also noted how the addition of mercuric chloride to low salinity samples may also result in low calculated then observed CO₂ concentrations.

“Because CO₂ concentrations do not change linearly during mixing, they were estimated using corresponding DIC and TA mixing values (Fig. 3C) (Jiang et al., 2008a).

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In the chemical model of the CO₂SYS, NH₃, NH₄⁺, and organic matter contribution to TA were not included (Cai et al., 1998; Cai et al., 2010b), which were likely high in low salinity waters. Thus, lower calculated CO₂ than observed CO₂ was expected as the observed TA included other acid-base components (Fig. 3C). Another factor that may contribute to the lower calculated CO₂ than observed CO₂ could be the use of mercuric chloride as a preservative in low salinity samples (S < 10) (Trabalka and Reichle, 2013). Excess alkalinity generated via the dilution of mercuric chloride could contribute to conservative CO₂ flux estimates (Trabalka and Reichle, 2013) although due to the relatively high TA in the Delaware River we believe this effect is small.”

— Results

— Page 10910 Line 21-25: Why different time ranges for discharge and temperature? Directly mention differences in the data record.

I felt that the variability in monthly mean water temperatures could be sufficiently captured within the past 10-year average records. However, due to the irregularity of weathering and various external events, river discharge fluctuations are much larger from year to year than monthly mean surface water temperatures. Thus, I believe a longer 30-year monthly discharge record is necessary to capture the general trend and range of seasonal river discharge rates.

“Measured surface water temperatures and river discharge during each cruise were compared with the 10 year (2004-2014) and 30 year (1980-2014) monthly averages for surface water temperatures and Delaware River discharge rates, respectively.”

— Page 10911 Line 1: Change “The Delaware River discharged...” to “The Delaware River discharge...”

Now the sentence is, “The Delaware River discharge was greatest during March 2014 and June 2013.”

— Page 10912 Line 10: Difficult to see any DIC drawdown relative to salinity in

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Figure 2a that would also indicate a bloom... unusual for such a strong bloom. If entire water column/estuary was affected by the bloom, how does this affect your calculation of the DIC endmember? Since much of the seasonal cycle you describe relies on this point, the biological production should be better shown or explained.

Agreed. I have added some research on variability of DIC at the end-members. It appears that for the most part, precipitation rates are the dominant controlling processes effecting DIC variability at the river end-member with minimal impact from biological activity. This is actually expected as river DIC and TA are largely a dilution of weathering production by rain (Cai et al., 2008).

“With much of the DIC pool dominated by carbonate and bicarbonate ions, Sharp et al., (2009) observed small seasonal influences on DIC concentrations due to temperature affects and biological activity. They suggest that the majority of variability in DIC in the upper tidal river of the Delaware Estuary is due to the combined interaction of varying precipitation rates and prior meteorological conditions. This is expected as river DIC and TA are largely a dilution of weathering production by rain (Cai et al., 2008). On the other hand, at higher salinities, any drawdown of DIC relative to salinity is small since less than 1% of the DIC pool exists as pCO₂ (Sharp et al., 2009). Thus, while total DIC concentrations illustrate some fluctuations in biological activity (which occurred mostly at the highly productive mid-bay), it is an integrated measurement of freshwater and seawater mixing (Sharp et al., 2009).”

— Page 10913 Section 3.4: Temporal questions here could be better addressed, such as definition of seasons as well as the temporal averaging for the annual estimates.

Good point. I have defined each season and given annual estimates for each of them.

“The seasonal variation between pCO₂ values was largest at low salinities around 0 to 5 with pCO₂ values in the summer (June, July, and August) nearly two-fold greater than those observed in the spring (March) and fall (October and November) seasons (Fig. 7). . . .” “In winter (December), pCO₂ values were always supersaturated with respect to

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the atmosphere across the entire salinity range.”

“Seasonally, the Delaware Estuary served as a strong CO₂ sink (-5.0 ± 6.0 mol-C m⁻² yr⁻¹) in the spring, a strong source (4.9 ± 8.1 mol-C m⁻² yr⁻¹) in the summer, a weak source (1.0 ± 2.4 mol-C m⁻² yr⁻¹) in the fall, and a strong source (5.7 ± 1.9 mol-C m⁻² yr⁻¹) in the winter. While low salinity waters were strong CO₂ sources, proportionally these upper regions ($0 \leq S < 10$) were small in comparison to the total estuarine study area. In turn, their area-averaged contribution (27.1 ± 6.4 mol-C m⁻² yr⁻¹) to overall regional flux (2.4 ± 4.8 mol-C m⁻² yr⁻¹) is minor. Thus, the Delaware Estuary as a whole acts as a relatively weak CO₂ source (2.4 ± 4.8 mol-C m⁻² yr⁻¹), which is in great contrast to many river estuaries that are strong CO₂ sources (26 ± 21 mol-C m⁻² yr⁻¹) (Borges and Abril, 2011).”

— Page 10914 Line 13/14: How does this bloom timing relate to other observations of the seasonal biological cycles in the Delaware Estuary?

Good question. I've added a little more information about historical production data to the discussion section as shown below.

“For example, in the urban river and turbidity maximum zones ($S < 5$), high pCO_{2obs} at 12.7 °C in the spring and winter may reflect both river inputs and strong respiratory CO₂ production. Low pCO_{2obs} at 12.7 °C during the warmer months likely reflect the removal of CO₂ due to various non-thermal processes. During the warmer months from May to October, Yoshiyama and Sharp (2006) found elevated nitrite (NO₂) concentrations in the urban river when nitrification and primary production were highest. In addition, high NO₂ concentrations were observed in the mid-bay in summer when primary production was maximal (Pennock and Sharp, 1994). Comparably, pCO_{2mean} at Tobs (changes due to the seasonal thermal cycle) trends were opposite to that of pCO_{2obs} at 12.7 °C with lower than pCO_{2obs} values in the winter and higher than pCO_{2obs} values in the summer. These opposing signals suggest that increases in surface water pCO₂ due to winter-to-summer warming are partially compensated by

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the reduction of surface water pCO₂ due to mixing processes and/or biological removal of CO₂ (Takahashi et al., 2002). Sharp et al. (2009) found that during the March-April period ammonium (NH₄), phosphate (PO₄), and silicate (Si) concentrations were heavily depleted in the mid and lower bay regions due to extensive spring blooms. Similarly, but in the opposite direction, the reduction in surface water pCO₂ due to fall-to-winter cooling is partially compensated by the elevation of surface water pCO₂ caused by various non-thermal processes (Fig. 8)."

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— Page 10915 Appendix B could be expanded and would be a worthy inclusion in the main paper.

It appears that the need for Appendixes is probably unnecessary (similar comments made by other referee) since space is not a critical issue for Biogeosciences. I have included both Appendixes back into the main paper and tried to make some expansions for clarification.

"We further examine the relative importance of the temperature and biological effects in each salinity interval by calculating the ratio of ΔpCO_{2temp} to ΔpCO_{2bio} (T/B). Using similar methods as performed in Takahashi et al., (2002), we calculate the thermal effects on surface water pCO₂ in each salinity interval as follows:

$$\Delta pCO_{2thermal} = (pCO_{2mean} \text{ at } Tobs)_{max} - (pCO_{2mean} \text{ at } Tobs)_{min} \quad (12)$$

where $(pCO_{2mean} \text{ at } Tobs)_{max}$ and $(pCO_{2mean} \text{ at } Tobs)_{min}$ are the maximum and minimum pCO_{2mean} at $Tobs$ values, respectively. In other words, the thermal effects on the mean annual pCO_2 value is represented by the seasonal amplitude of $(pCO_{2mean} \text{ at } Tobs)$ values computed using Eq. (7). Likewise, the non-thermal effects (biological and mixing processes) on surface water pCO_2 were calculated as follows (Takahashi et al., 2002):

$$\Delta pCO_{2non-thermal} = (pCO_{2obs} \text{ at } 13.3^\circ C)_{max} - (pCO_{2obs} \text{ at } 13.3^\circ C)_{min} \quad (13)$$

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where ($p\text{CO}_2^{\text{obs}}$ at $13.3\text{ }^{\circ}\text{C}$) $_{\text{max}}$ and ($p\text{CO}_2^{\text{obs}}$ at $12.7\text{ }^{\circ}\text{C}$) $_{\text{min}}$ are the maximum and minimum $p\text{CO}_2^{\text{obs}}$ at $12.7\text{ }^{\circ}\text{C}$ values, respectively. Thus, the non-thermal thermal effects on surface water $p\text{CO}_2$ ($p\text{CO}_2^{\text{obs}}$ at $13.3\text{ }^{\circ}\text{C}$) is represented by the seasonal amplitude of $p\text{CO}_2$ values corrected to the annual mean temperature using Eq. (6). The relative importance of these effects in each salinity interval can be expressed as the difference between $\Delta p\text{CO}_2^{\text{thermal}}$ and $\Delta p\text{CO}_2^{\text{non-thermal}}$ ($T - B$) or the ratio of $\Delta p\text{CO}_2^{\text{thermal}}$ to $\Delta p\text{CO}_2^{\text{non-thermal}}$ (T/B). In estuarine regions where thermal effects on surface water $p\text{CO}_2$ exceed non-thermal effects, the (T/B) ratio is greater than 1 or ($T - B$) is positive, whereas in areas where non-thermal effects dominate, the (T/B) ratio is less than 1 or ($T - B$) is negative.

— Summary and Concluding Remarks

— Page 10919 Line 6: Great statement! Belongs at the top of the paper.

“While this study serves as the first air–water CO_2 flux product in the Delaware Estuary, there are several limitations.”

Thanks! I have included this in the beginning of the new caveats sections (please see 4.4 Assumptions and limitations)

— Page 10919 Line 6-16: This section needs to be broadly expanded to turn it into an appropriate assumptions and caveats section (consider it section 4.4). Some of the points made here could then receive more attention, such as some review of how nearby marshes might influence $p\text{CO}_2$

Please see new 4.4 Assumptions and limitations section

— Tables and Figures

— Table 1. Area-weighted average flux in an additional column.

Taking into consideration responses from both referees, I have made some significant changes to Table 1 (now Table 2). First, I split the data into two tables. One showing

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area-averaged pCO₂ and CO₂ flux and the other showing estimated flushing times for each zone. Second, I have added standard deviation and range for each section to help strengthen the results.

— Figures 1-9. In general, sizing here could be made a little more uniform. In some cases text sizes were extremely difficult to read (see especially the legends in Figures 7 and 9). Increasing the size of Figure 2 might also be able to highlight any potential DIC drawdown influencing biological production.

I agree. I was also a little disappointed in the “readability” of the figures. I will try to increase figure and text sizes.

— Figure 2. Panel c not discussed in manuscript.

I have included some discussion of Fig. 3C in the manuscript. Please see response (Page 10910 Line 15).

— Figure 4, 5. ODV stamp required on figures generated using that program, as well as a Schlitzer citation.

I have included ODV stamps and Schlitzer citations to Figures 4 and 5.

— Figure 7. Not sure this is the best way to show differences between temperature and biological forcing, salinity binning aside. Firstly, the variables need better labels (use T and B as in Appendix B) and the pCO₂(obs) line should be the boldest. I would also consider plotting T and B as anomalies from pCO₂(obs), or showing a vector diagram, or using color to highlight times when warming, cooling, production, and respiration are clearly factors so that the interpretation of this figure immediately jumps out.

I have made pCO₂(obs) line the boldest. To help highlight times of addition (red) or removal (blue) of CO₂, I have inserted colored arrows. Moreover, each arrow is accompanied with either a T or B symbol to indicate whether this pCO₂ change was governed by thermal or non-thermal processes.

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Please also note the supplement to this comment:
<http://www.biogeosciences-discuss.net/12/C5056/2015/bgd-12-C5056-2015-supplement.pdf>

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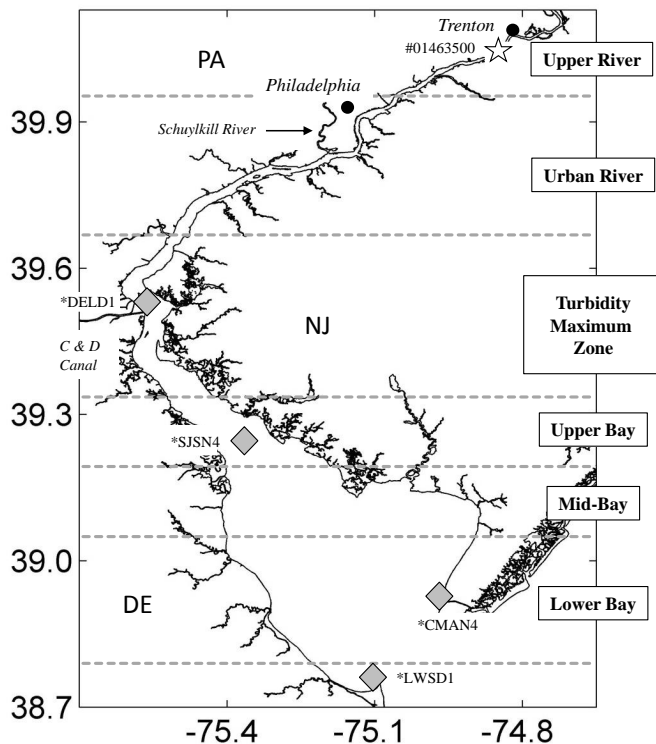
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Fig. 1. Map of the Delaware Estuary divided into six zones from the head of the tide in Trenton, NJ to the mouth of the bay as defined in Sharp et al. (2009).

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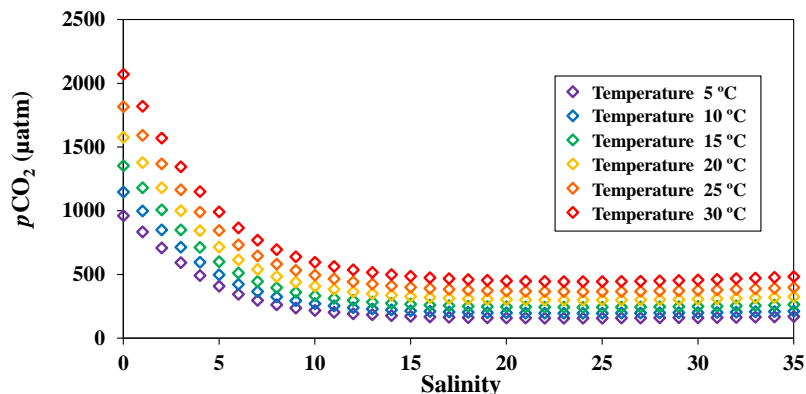


Fig. 2. Simulated surface water $p\text{CO}_2$ against salinity grouped by temperature bins. Surface water $p\text{CO}_2$ values were calculated using river and ocean end-member TA and DIC values of 900 and 960 $\mu\text{mol kg}^{-1}$ and 230

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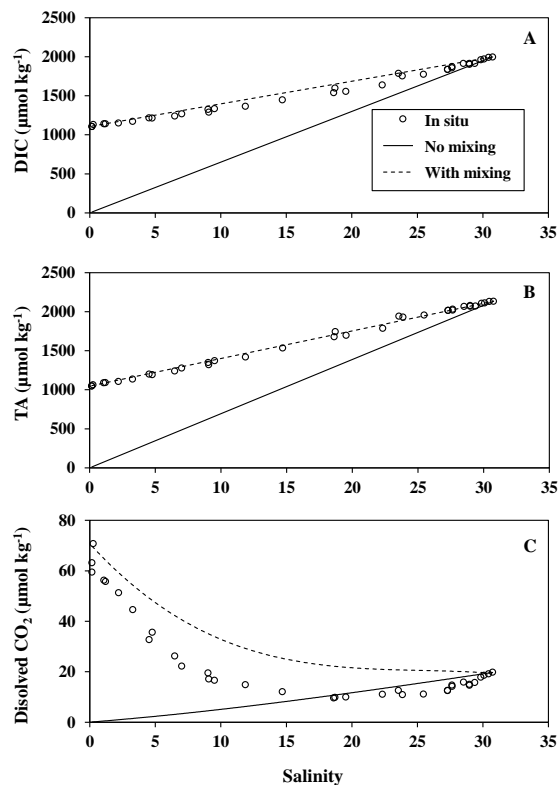


Fig. 3. Concentrations of (A) DIC, (B) TA, and (C) dissolved CO₂ in the Delaware Estuary during March 2014. Open circles represent in situ concentrations. Solid lines represent values after the ocean end-memb

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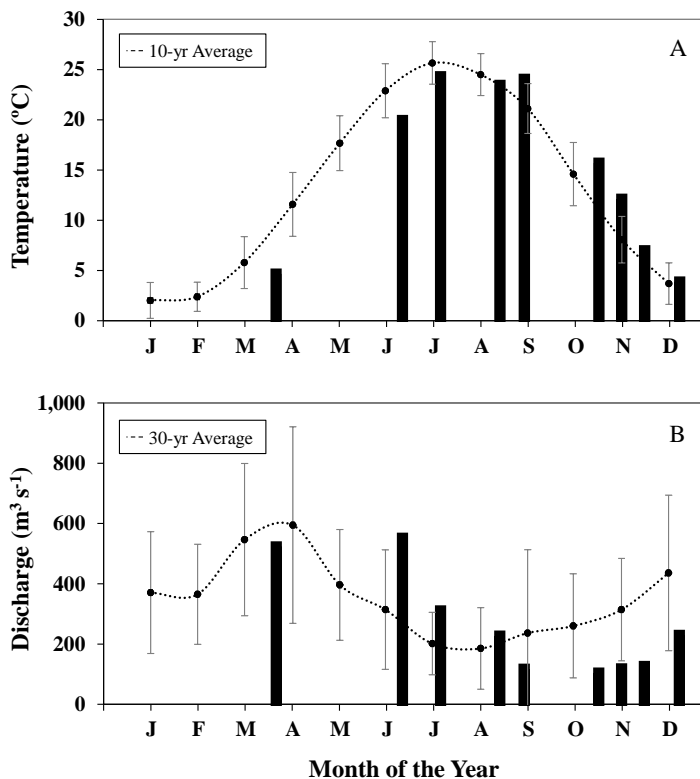


Fig. 4. (A) Surface water temperatures and (B) Delaware River discharge rates recorded in the Delaware Estuary during each sampling month. Error bars represent standard deviations of the 10-year (2004-2014) a

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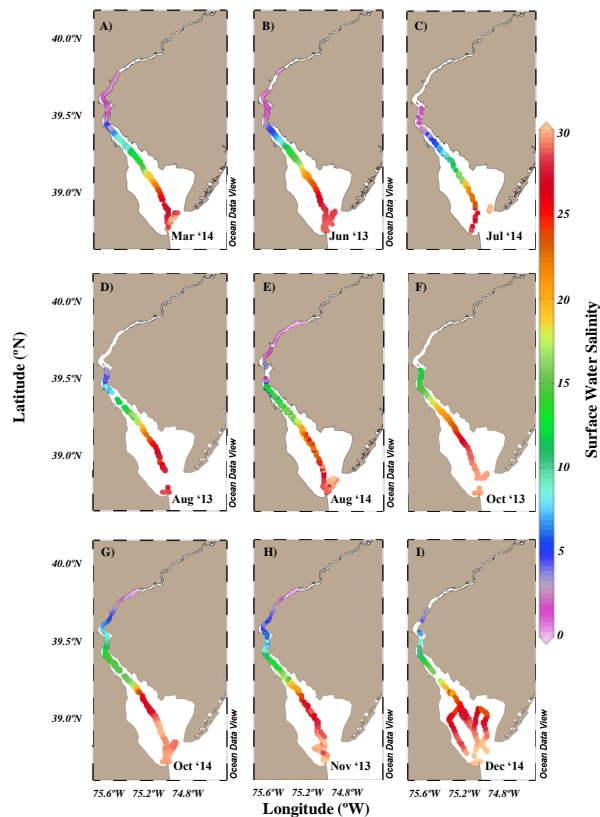


Fig. 5. Spatial distributions of surface water salinity in the Delaware Estuary measured during each sampling month. The map was designed with the ODV software by R. Schlitzer (Ocean Data View software, 2015,

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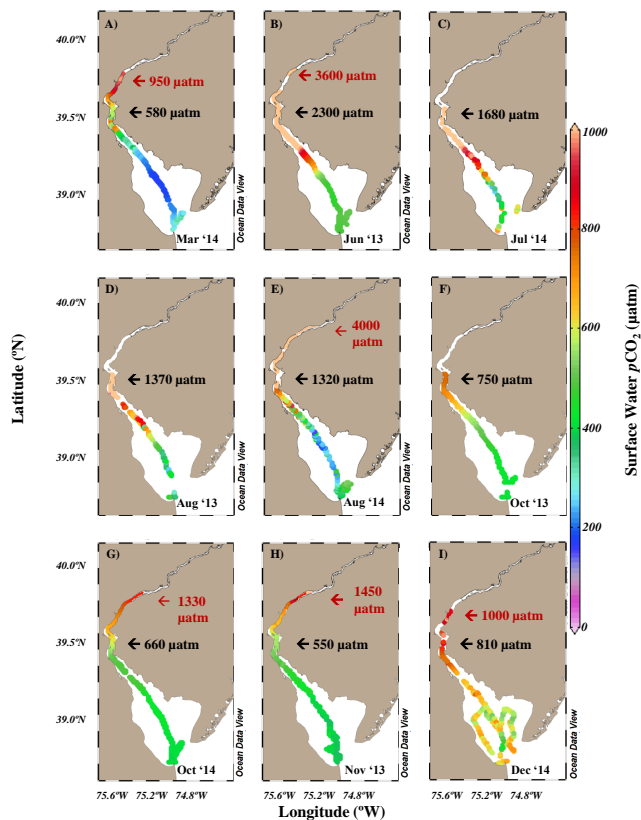
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Fig. 6. Spatial distributions of surface water $p\text{CO}_2$ in the Delaware Estuary measured during each sampling month. Black and red arrows show surface water $p\text{CO}_2$ values at the Chesapeake-Delaware Canal and the no

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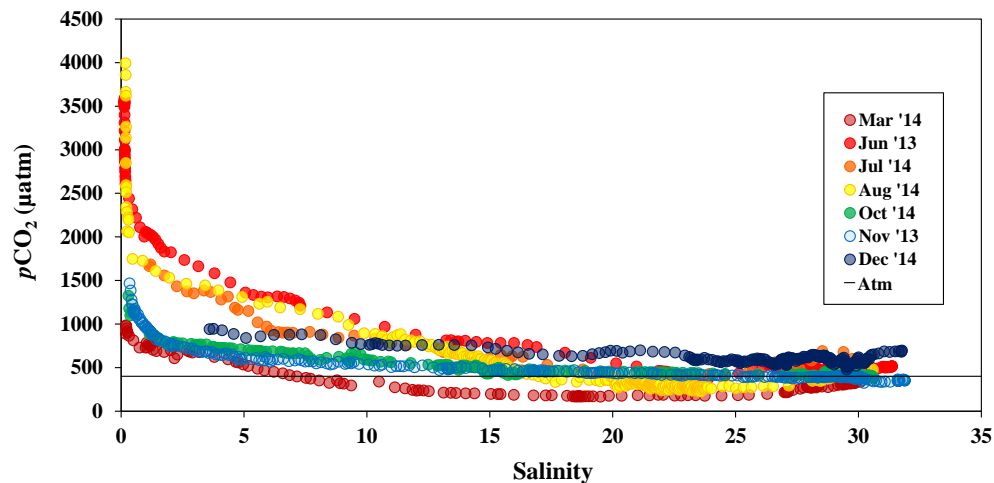



Fig. 7. Measured surface water pCO₂ against the salinity gradient during each sampling month in the Delaware Estuary.

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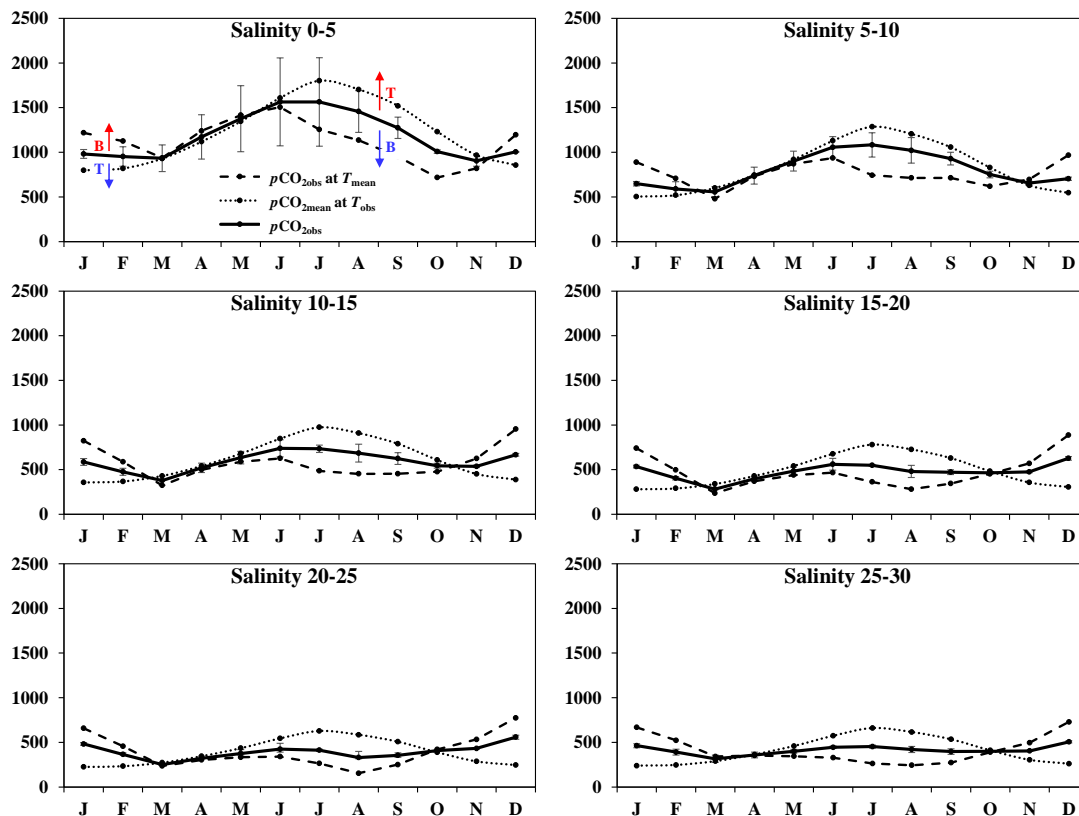


Fig. 8. Salinity-binned intervals of temperature-normalized observed $p\text{CO}_2$ values at 13.3°C , annual mean, area-averaged $p\text{CO}_2$ values at in situ temperature, and observed $p\text{CO}_2$ values in the Delaware Estuary over

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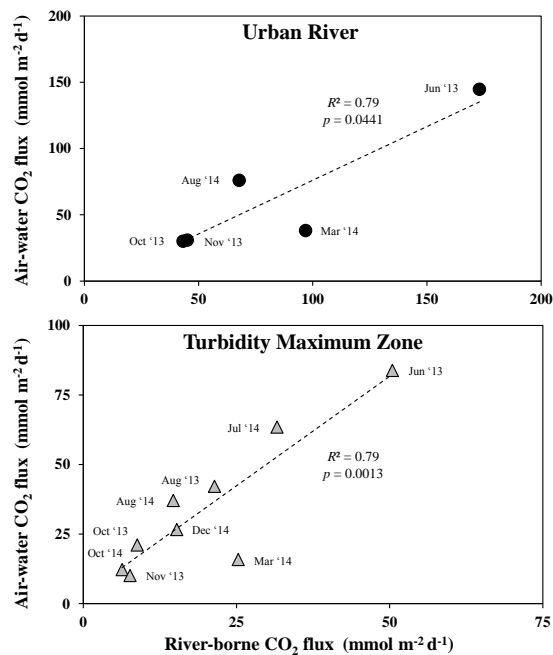
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Fig. 9. Air-water CO₂ fluxes against river-borne CO₂ fluxes in the urban river and turbidity maximum zone of the Delaware Estuary. Note the different axes used for the urban river and turbidity maximum zone.

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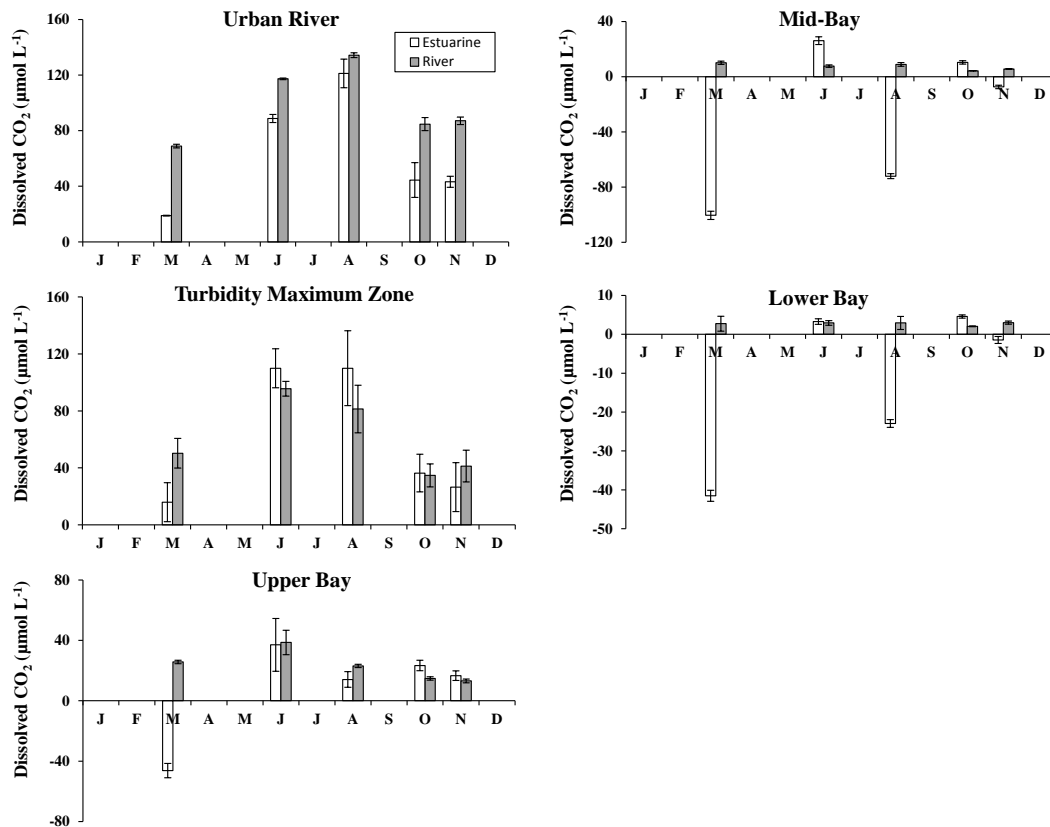


Fig. 10. Dissolved CO₂ concentrations (normalized to 13.3 °C, area averaged) due to river inputs and internal estuarine sources in each region of the Delaware Estuary. Note the different axes used across all r

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